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# EMISSION OF HYDROCARBONS TO THE ATMOSPHERE FROM COOLING TOWERS

Frank Bonamassa, et al

Joint District Federal and State Project for the Evaluation of Refinery Emissions

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JOINT DISTRICT, FEDERAL AND STATE PROJECT
FOR THE EVALUATION OF REFINERY EMISSIONS

REPORT NUMBER 5
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# EMISSION OF HYDROCARBONS TO THE ATMOSPHERE FROM COOLING TOWERS

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Details of illustrations in this document may be better studied on microfiche.

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## FOREWORD

In August 1955, the Los Angeles County Air Pollution Control District, the California State Department of Public Health, and the U. S. Public Health Service inaugurated the Joint District, Federal, and State Project for the Evaluation of Refinery Emissions in Los Angeles County. The Western Oil and Gas Association, representing the petroleum industry, also participated in the project. This report presents the results of one of the studies of the Joint Project.

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# EMISSION OF HYDROCARBONS TO THE ATMOSPHERE FROM COOLING TOWERS

IN BRIEF:

Cooling towers in petroleum refineries are a source of hydrocarbon emissions to the atmosphere when the cooling water acquires hydrocarbons in leaking heat exchangers and releases them when passing through the tower. A sampling procedure and an analytical method were developed to measure the hydrocarbon concentration of the water before and after its pass through the cooling tower. Tests revealed that of the 93 cooling towers operating in Los Angeles County, 17 showed detectable emissions totaling about three tons of hydrocarbons per day.

# INTRODUCTION

Petroleum refineries use large quantities of water for cooling, and before the water can be reused, the heat absorbed must be removed. One of the simplest and oldest known methods to cool water is to evaporate a portion of the liquid by exposing its surface to the air, resulting in a sensible heat loss from the remainder of the liquid. The device in widespread use in the petroleum refineries of Los Angeles County for exposing a surface of the cooling water to the air is the cooling tower (Figure 1).

In the cooling tower, water is pumped to the top of the tower where it is discharged through a distribution system. As the water cascades through the tower, it is continually diverted and redistributed by a series of decks and slat-type grids, thus constantly exposing new water surfaces to the air passing through the tower. In an atmospheric, or natural draft, tower prevailing winds are relied upon for ventilation. In the mechanical draft tower, fans are employed to provide the air movement. Both the atmospheric and the mechanical draft towers are capable of cooling water to the same minimum temperature.

Sizes of cooling towers in petroleum refineries depend on several factors--chiefly the type of draft and the amount of cooling water circulated. The cooling towers considered in this report varied in their water circulation rates from 200 to 40,000 gallons per minute.

The circulating cooling water may contain some hydrocarbons in addition to certain substances added to the water to deter the growth of algae, retard corrosion, or minimize other undesirable effects. These hydrocarbons, existing in the water either in a dissolved state or as discrete entrained globules, can enter the cooling water as it passes through a leaking heat exchanger or condenser. When the cooling water subsequently passes through the tower, these hydrocarbons may escape into the atmosphere. It is the purpose of this study to ascertain the magnitude of these emissions.

A census of the cooling towers in the petroleum refineries of Los Angeles County revealed that there were 93 cooling towers in operation; 71 of these were located in the six major refineries. Over 700,000 gallons of cooling water are circulated per minute in these towers with the six major refineries accounting for approximately 95 per cent of the total. Cooling tower circulation rates varied from 200 to 40,000 gallons per minute, with 50 per cent of the towers having circulation rates in the 5,000 to 15,000 gallons per minute range.

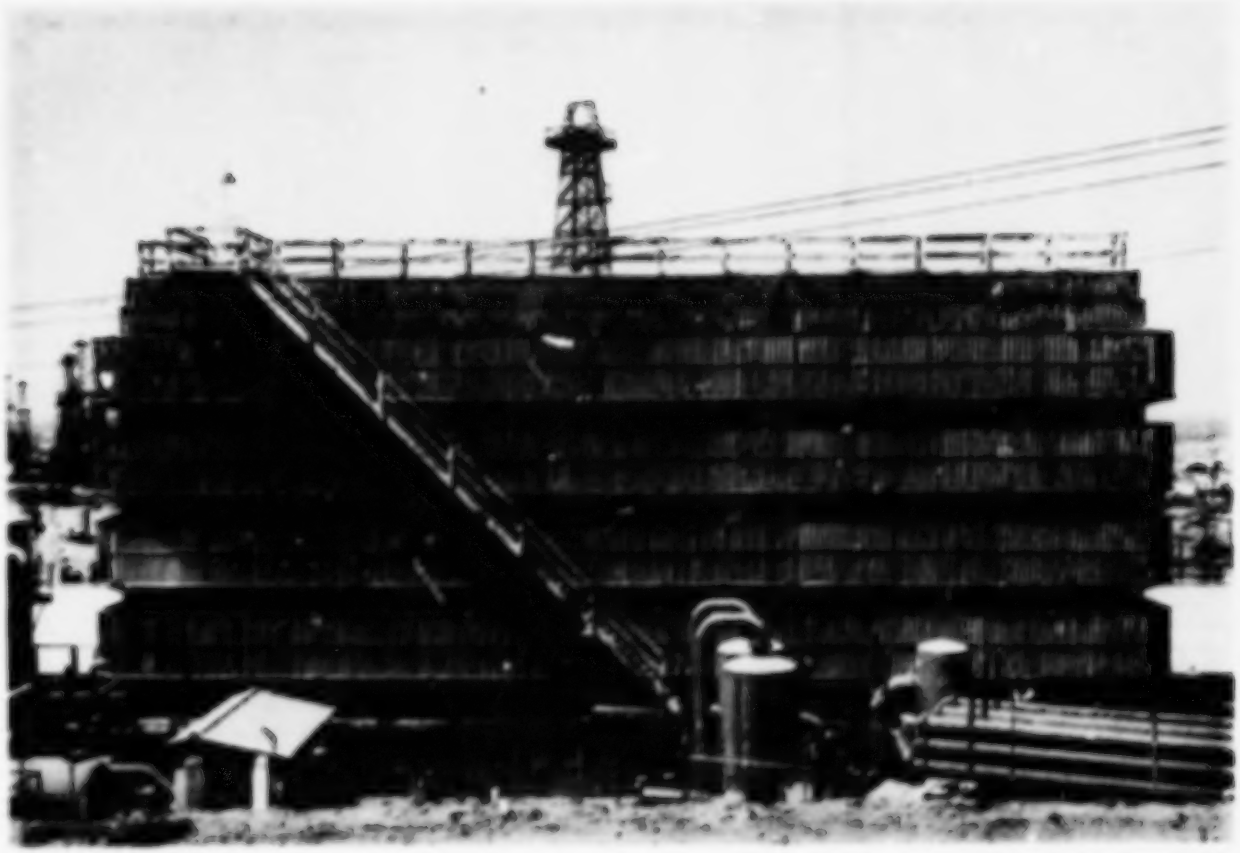


Figure 1. Cooling tower.

Since the total number of cooling towers was reasonably small, it was decided to test every one of the towers for hydrocarbon emissions provided a means of sampling could be devised that would not place severe demands on the staff of the Joint Project from the standpoint of time and personnel required.

## SAMPLING PROCEDURE

At first, means were considered of sampling the atmosphere for hydrocarbons in the immediate vicinity of a cooling tower. This idea was abandoned because it would have been extremely difficult to select a representative sampling point since the steam plume was being emitted from various elevations and locations on the tower depending on the local wind conditions, type of draft supplied, and water circulation rate; nor was it likely that concentrations of hydrocarbons were uniform throughout the plume.

Attention was then directed toward determining the hydrocarbon emissions by sampling the cooling water directly by drawing a continually metered sample of the inlet water to the tower and passing it at low rate through a 13-gallon carboy where liquid and gaseous hydrocarbons were allowed to separate from the water. At the end of the sampling period, usually seven days, the volume of the gaseous phase was measured and the concentration of hydrocarbon determined by an infrared spectrophotometer. The liquid hydrocarbon phase was decanted from the carboy and the low-boiling fraction extracted by steam distillation. (The sum of the hydrocarbons in the liquid and gaseous phases was assumed to represent the hydrocarbons lost to the atmosphere.) Using this method, nine tests were performed on six cooling towers.

These preliminary tests indicated that hydrocarbon emissions did occur, but the data were subject to several limitations in the sampling procedure. Hydrocarbon loss from the carboy due to solubility in the water was neglected. Depending on the type of hydrocarbon, this loss might have been appreciable. Investigation further disclosed that minute droplets of hydrocarbons might remain suspended in the body of the water for a period of six hours or more. In the method used, these hydrocarbons would be carried out and not measured. Another factor which prompted the search for a better method was the long sampling time required.

A revised sampling procedure was developed which consisted of taking grab samples of the cooling tower water both before and after it had passed through the tower. Consideration of the difference between the hydrocarbon concentration in the two samples, and water circulation rate through the tower, could allow the determination of the hydrocarbon emissions to the atmosphere.

In obtaining a sample of the cooling water entering the tower, several precautions must be taken. Since it is customary for a single cooling tower to serve many heat exchangers, it is necessary to obtain a sample at a point in the return line to the tower downstream from the last heat exchanger to insure that no additional hydrocarbons have been acquired after the sampling point. The sampling tap should also be located where stratification of the fluid is at a minimum, as at a vertical riser or a centrifugal pump casing. Most refineries have bleed lines suitable for sampling located at places which meet these requirements.

Before drawing the sample of inlet cooling water, the valve at the sampling point is fully opened and water allowed to flow to clear the line of any dirt which may have accumulated. After several minutes of maximum flow, the valve is closed, and a 60-ml. glass Mine Sampling Tube is connected to it with tight-fitting rubber tubing and any reducing fittings which may be required (Figure 2). Then, with both stopcocks on the Mine Sampling Tube opened, the valve at the sampling point is opened slightly and the tube allowed to fill and overflow. After uniform flow has been established through the sampling tube, the valve at the sampling point and then the tube stopcocks are closed and the sample tube removed.

Samples of water leaving the cooling tower are obtained by inserting a glass funnel at the end of a probe directly into the dripping water just above the collecting basin at the foot of the tower. Flexible tubing conducts the water caught by the funnel to a small Erlenmeyer flask (Figure 3).

## ANALYTICAL METHOD

The Mine Sampling Tube containing the cooling tower inlet water sample is inserted into a stripping train consisting of a cylinder containing hydrocarbon-free nitrogen, rotameter, bubbler, Ascarite drying tube, and Shepherd cold trap immersed in a Dewar flask containing liquid oxygen. The sample tube is inserted into the stripping train between the rotameter and the bubbler (Figures 4 and 5). The sample is drained into the bubbler under a slight positive pressure of nitrogen. In this manner the loss of hydrocarbons from exposure of the sample to the atmosphere is avoided. The nitrogen gas stream is then passed through the bubbler, drying tube, and cold trap for a period of 15 minutes at a flow rate of one liter per minute.

At the end of this time, the trap, still immersed in the liquid oxygen bath, is evacuated to a pressure of 50 mm. of mercury to prevent an excessive build-up of internal pressure when its contents warm up to room temperature. The hydrocarbons are then vaporized by immersing the trap in a water bath at 70-80°C and flushed with a stream of filtered air into the test cell of an infrared spectrophotometer where their absorption at a

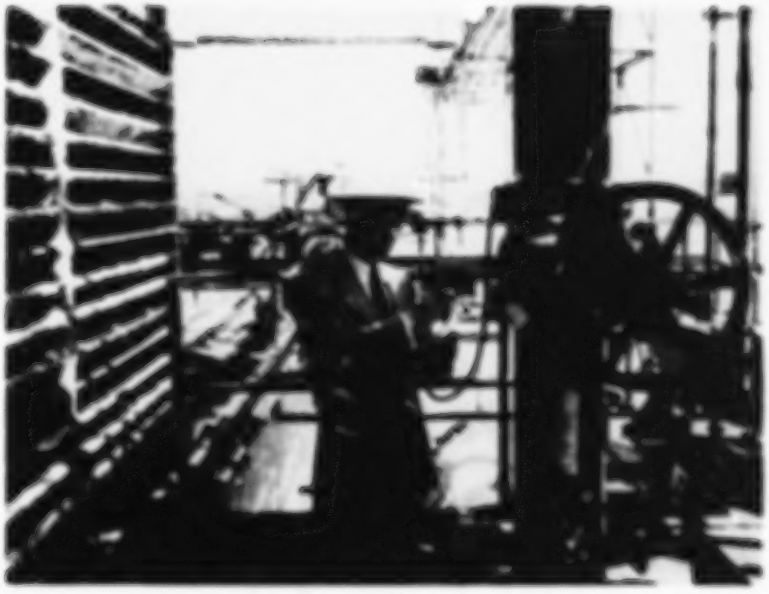
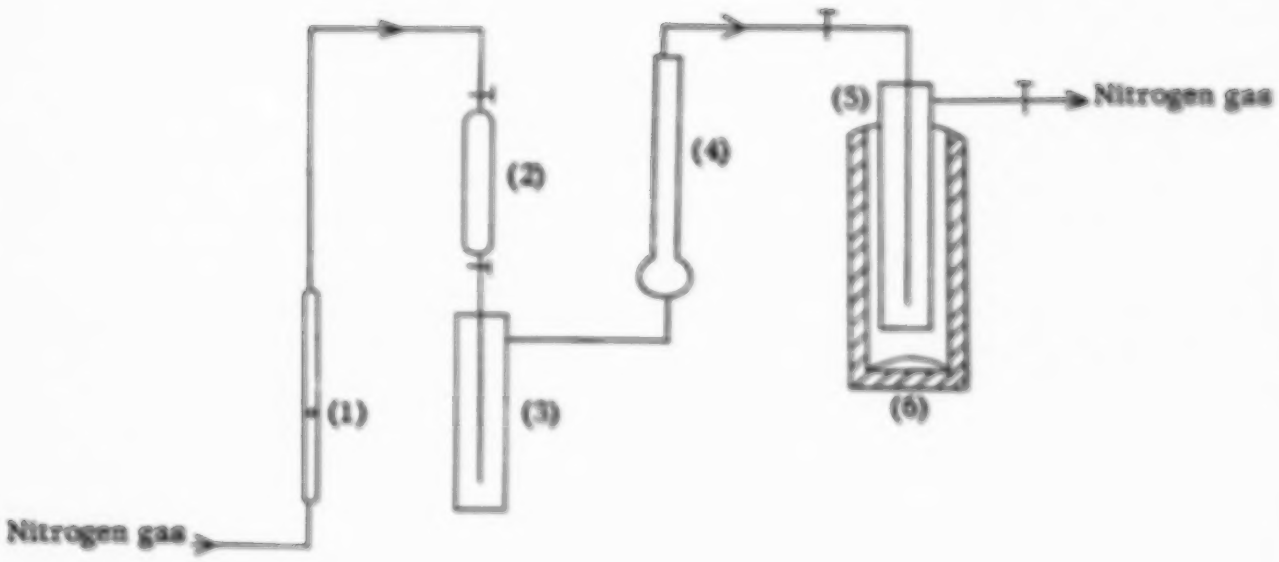


Figure 2. Obtaining sample of cooling tower inlet water.

Figure 3. Obtaining sample of cooling tower outlet water.

Figure 4. Flow sheet for stripping and collecting hydrocarbons from cooling tower water samples.




(1) Rotameter
(2) Mine Sampling Tube
(3) Bubbler
(4) Ascarite drying tube
(5) Shepherd cold trap
(6) Dewar flask containing liquid oxygen

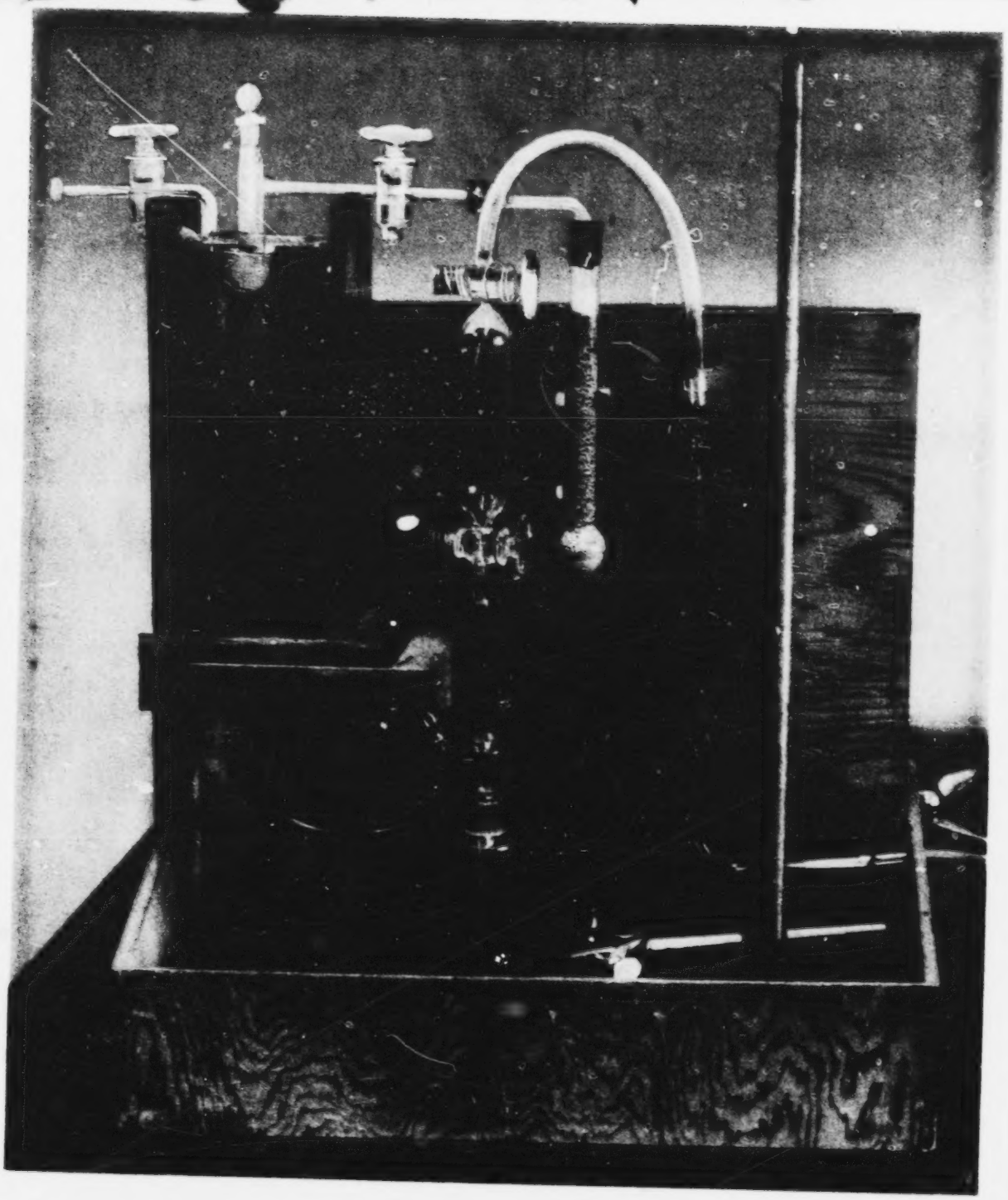


Figure 5. Apparatus for stripping and collecting hydrocarbons from cooling tower water samples.

wavelength of 3.45 microns is measured. The calibration curves of the infrared spectrophotometer are derived from known concentrations of normal hexane plotted as a function of per cent radiation transmitted at a wavelength of 3.45 microns. Therefore, the results of the spectrophotometric analyses are expressed in terms of n-hexane.

To analyze the hydrocarbon content of the cooling tower outlet water, a 60.0-ml. portion of the sample that was collected in the Erlenmeyer flask is pipetted into the bubbler and the stripping and spectrophotometric procedure followed as described above.

## Apparatus and Materials

Bubbler, fritted glass 125-ml. capacity.

Rotameter.

Ascarite drying tube, 20 cm length.

Ascarite 8 to 20 mesh.

Shepherd cold trap.

Dewar flask.

Mine Sampling Tube, 60 ml.

Vacuum pump.

Infrared Spectrophotometer, Beckman, Model 2A, equipped with a gas cell one meter in length with a capacity of one-half liter.

Liquid oxygen.

Compressed nitrogen (hydrocarbon-free).

Figure 4 shows a flow sheet for stripping and collecting hydrocarbons from cooling tower water samples.

## CALCULATIONS AND RESULTS

Table I, page 12, lists those towers from which emissions of hydrocarbons were detected. The emission from each tower is given by the following relationship:

$$E = KG\left[\frac{m_1}{v_1} - \frac{m_2}{v_2}\right]$$

Where:

E = emission of hydrocarbons, pounds per day

K = a conversion constant = $\frac{1440 \text{ min/day} \times 3785 \text{ ml/gal}}{454 \times 10^6 \text{ microgram / lb}} = 0.012$

G = cooling tower water circulation rate, gallons per minute

m = amount of hydrocarbons in water sample, micrograms

v = volume of water sample, milliliters

and subscripts 1 and 2 refer to inlet and outlet locations, respectively.

TABLE I

EMISSION OF HYDROCARBONS FROM COOLING TOWERS

| Cooling Tower No. | Water Circulation Gallons per Minute | Hydrocarbon Emission Calculated as n-hexane Pounds per Day |
|---|---|---|
| E-4 | 14,000 | 1570 |
| E-1w | 3,120 | 1400 |
| D-7 | 28,000 | 700 |
| C-6 | 3,000 | 616 |
| C-12w | 1,000 | 532 |
| B-7 | 14,000 | 318 |
| C-14 | 14,000 | 289 |
| C-14w | 12,000 | 239 |
| D-4 | 18,000 | 186 |
| K-1 | 1,000 | 147 |
| C-13 | 15,000 | 129 |
| C-18 | 10,000 | 56 |
| C-11 | 8,000 | 22 |
| I-2 | 1,800 | 10 |
| I-3 | 700 | 10 |
| N-1 | 1,000 | 8 |
| L-1 | 400 | 4 |
| | TOTAL (rounded) | 6200 |

## DISCUSSION

### Sampling Procedure

There are several configurations of cooling water systems in refineries which permit a portion of the hydrocarbons in the cooling water lines to avoid capture by the sampling procedure described. Occasionally the pump in a cooling tower heat exchanger circuit is placed in the return line to the tower, and since it is customary to use an open well as a pump intake, some of the hydrocarbons in the cooling water would escape to the atmosphere from the surface of the hot well. This situation can be rectified provided a sampling tap can be found upstream from the hot well.

Another arrangement whereby hydrocarbons escape capture is the installation in the inlet tower water line of an open condenser box. Here, the heat of condensation of the material contained within the condenser coils is removed by evaporating a portion of the cooling tower inlet water which is sprayed over the coils. Again, the remedy is to find a sampling tap upstream of the open condenser box.

Some cooling towers do not serve external heat exchangers, but have a cooling coil or bundle of coils built into the tower. Here, cooling is accomplished by having the water impinge directly on the coils during its fall through the tower. In these situations, it is possible that some hydrocarbons might escape into the atmosphere before a sample of the cooling water could be taken.

### Analytical Method

Duplicate cooling tower water samples containing hydrocarbon were collected from the same tower and run through the stripping train. Their resulting analyses by the infrared spectrophotometer have shown that the sampling, stripping, and freeze-out procedures are reproducible within the sensitivity of the spectrophotometric instrument.

In stripping cooling tower water samples, liquid oxygen (boiling point: -183°C) is used as a coolant to condense hydrocarbons. When water samples contain hydrocarbons lighter than $C_4$'s, such as methane, ethane, ethylene, acetylene, and propane, the freeze-out technique is not quantitative.

The present calibration of the Beckman Model IR 2A at the laboratory of the Air Pollution Control District is over the range of 67 to 483 (higher values are extrapolated) micrograms of normal hexane. The sensitivity of the instrument at the lower limit of the concentration range is ± 6.27 micrograms.

## Calculations and Results

Approximately 20 per cent of the cooling towers in service showed emissions or the presence of hydrocarbons. Although this is not a small percentage, no significant relationship was found between the size of the tower (based on the quantity of cooling water circulated) and the amount of emissions. Probably the sources of hydrocarbons in the cooling tower water are largely internal leaks in the heat exchangers served by the tower. Small leaks of this type often are not easily detected and frequently are extremely difficult to locate and repair. The large variety of heat exchangers usually served by a single tower is reflected in the wide range, from 3 to 1500 pounds per day, of emissions. Most likely, the chance that a given tower emits hydrocarbons is influenced by factors which are obscured by the multitude of operating conditions and process requirements.

As shown in Table I, page 12, the measured emissions of hydrocarbons to the atmosphere totaled about three tons per day. This amount is considered to represent the normal emission rate from all of the cooling towers under present operating conditions and maintenance practices. Although the emission rate from any single tower varies as leaks in heat exchangers develop, are detected and repaired, the total leakage in all the heat exchangers at any given time probably remains fairly constant since the new leaks arising balance the old leaks being repaired.

## CONCLUSIONS

Hydrocarbon emissions to the atmosphere from cooling towers of petroleum refineries in Los Angeles County amount to about three tons per day.

Of the 93 cooling towers tested, 17 showed detectable emissions of hydrocarbons.

The amount of emissions from a tower is largely determined by the properties of fluids and operating conditions within the heat exchangers served.

The sampling and analytical techniques evolved from this study provide a practical method for measuring the emissions of hydrocarbons to the atmosphere from cooling towers.